Weak Acids: Titration Curves, **Buffers**, and the **Henderson-Hasselbach Equation**

T08D10 – Unit Exam on Tuesday

Acid-Base Definitions

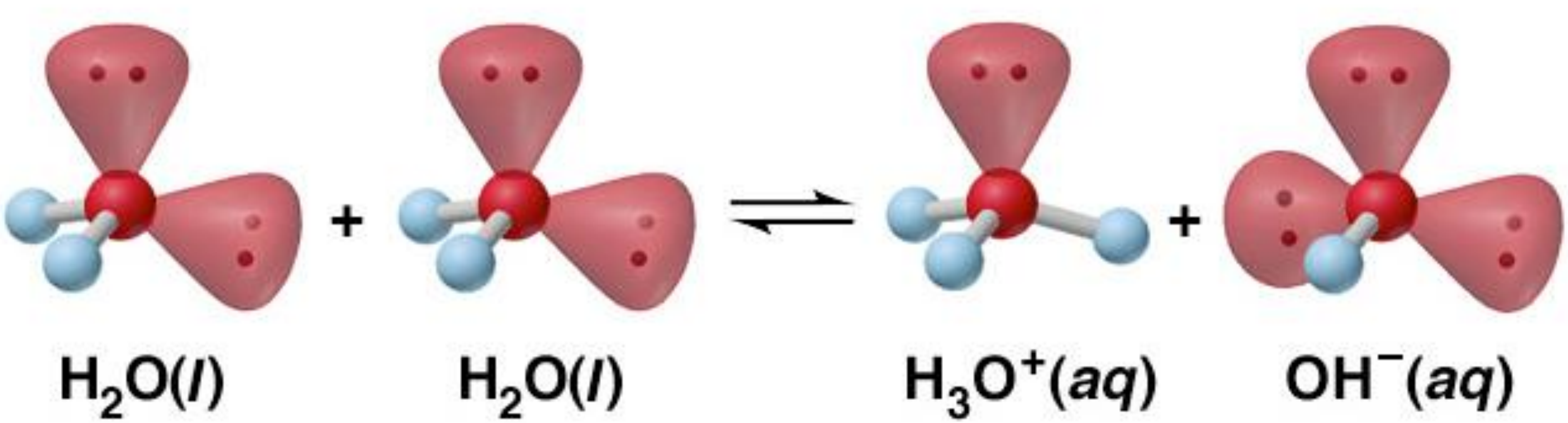
Acids

- generate H^+ in water
- H^+ donors
- excess H^+

Bases

- generate OH^- in water
- H^+ acceptors
- Excess OH^-

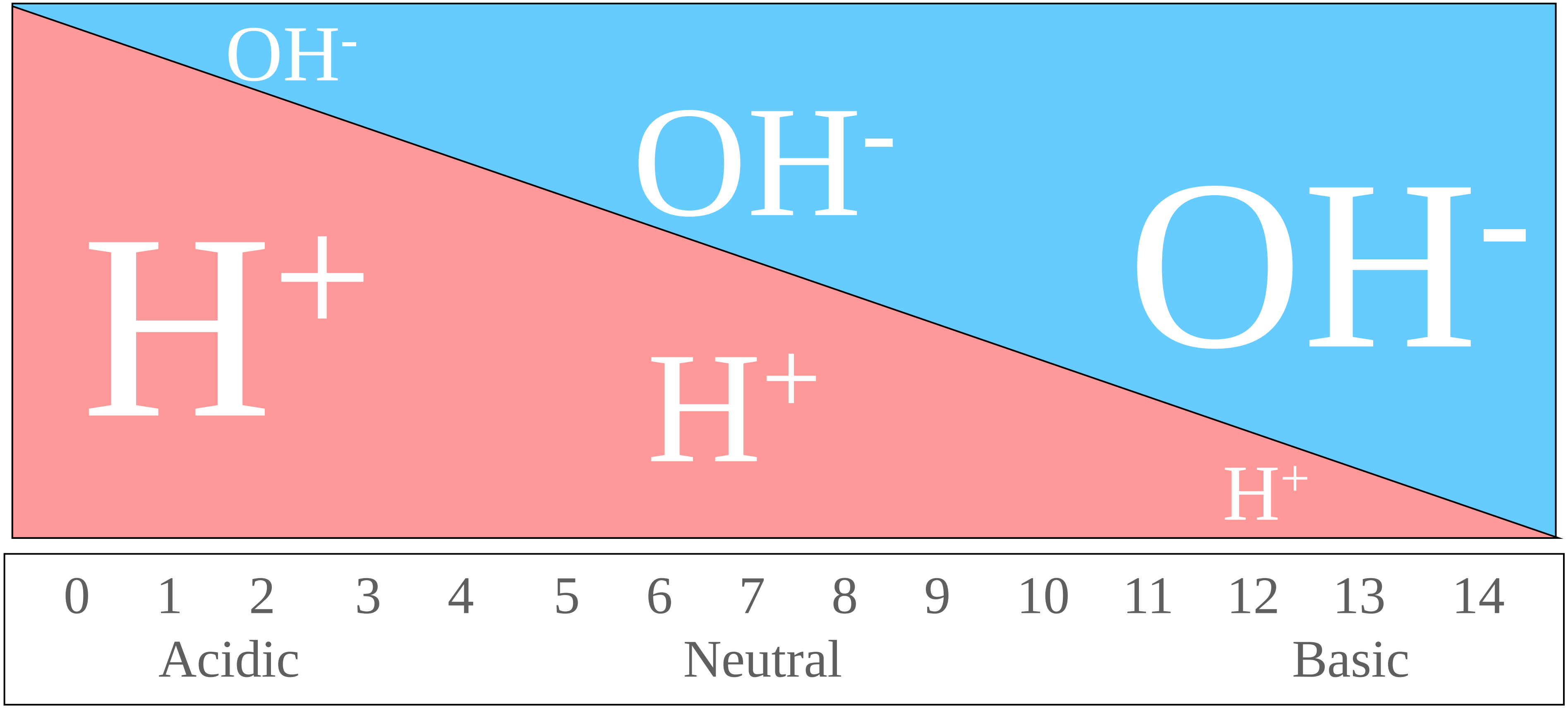
Equilibrium in Water



$$\boxed{K_{eq} = K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1\times 10^{-14}_{@25^o}}$$

Small K ≡ equilibrium favors reactants

As $[H^+]$ rises, $[OH^-]$ falls



H^+ and pH

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

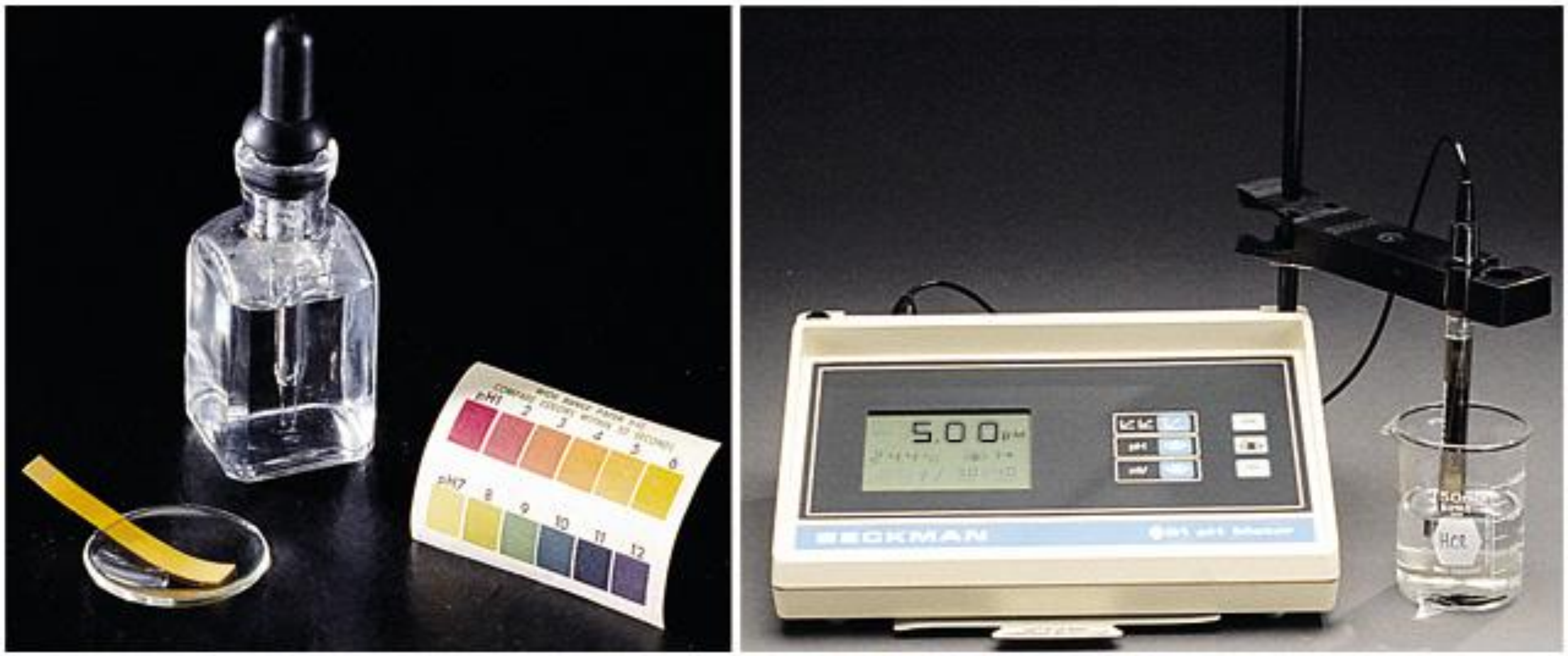
$$\boxed{[H^+] = \frac{K_w}{[OH^-]}} \qquad \boxed{pH = -\log [H^+]}$$

$[H^+]$	1×10^0	to	1×10^{-14}	in water
pH	1	to	14	in water

Relationships

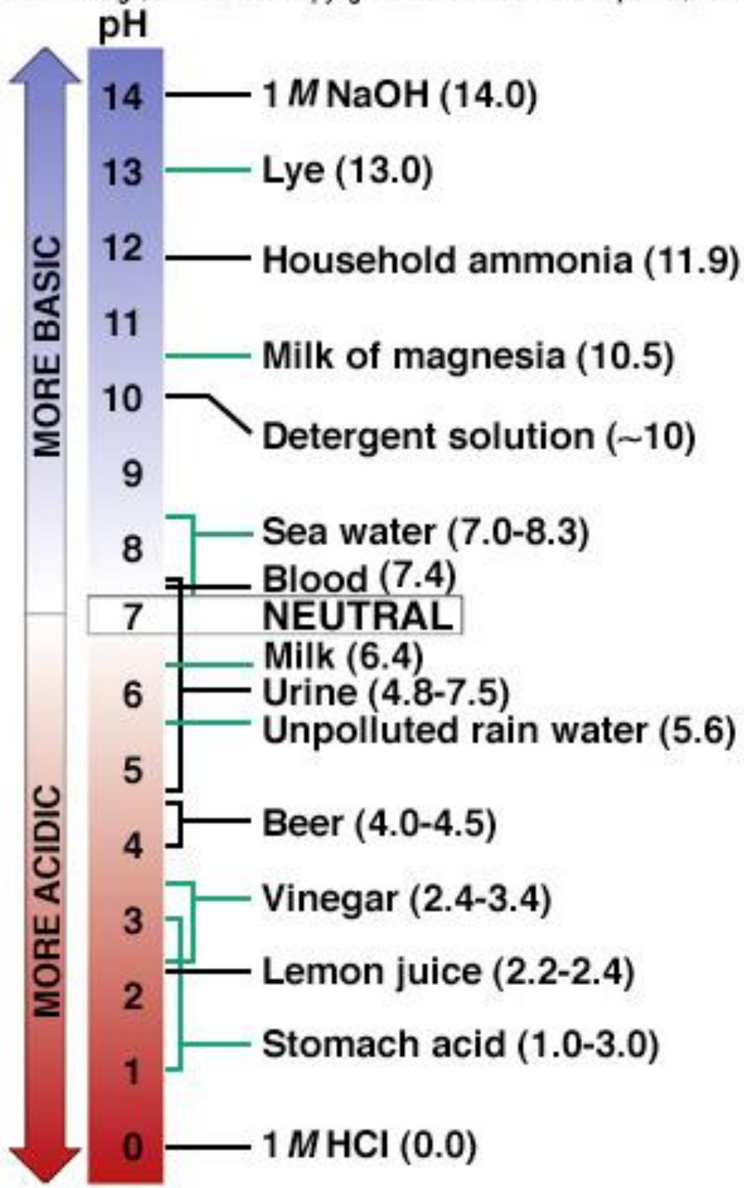
H^+	H_2O	OH^-
$[H^+] > [OH^-]$	$[H^+] = [OH^-]$	$[H^+] < [OH^-]$
Acidic solution	Neutral solution	Basic solution
$pH < 7$	$pH = 7$	$pH > 7$

Methods for Measuring pH



A B

Some pH Values

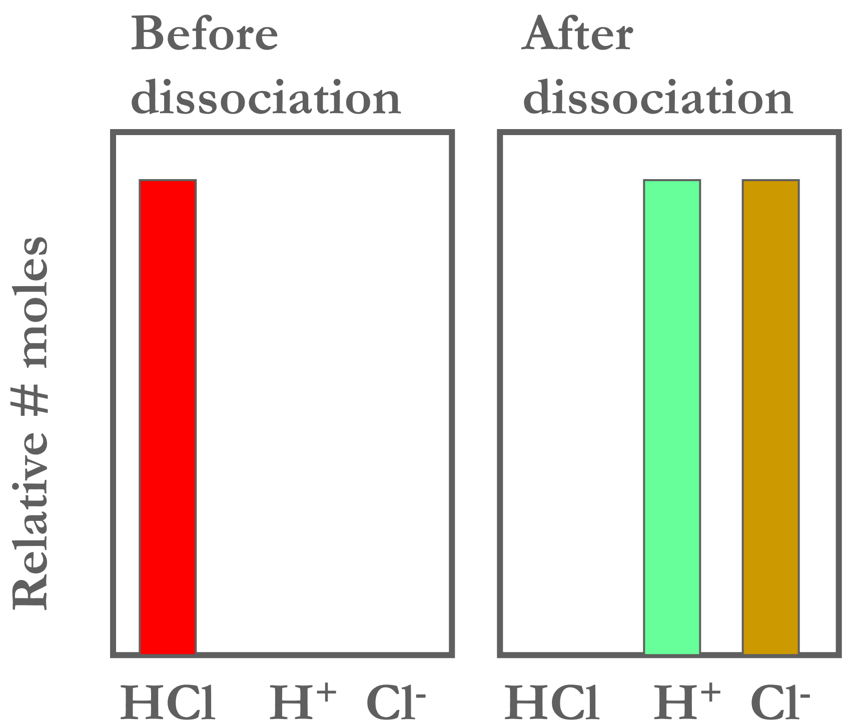


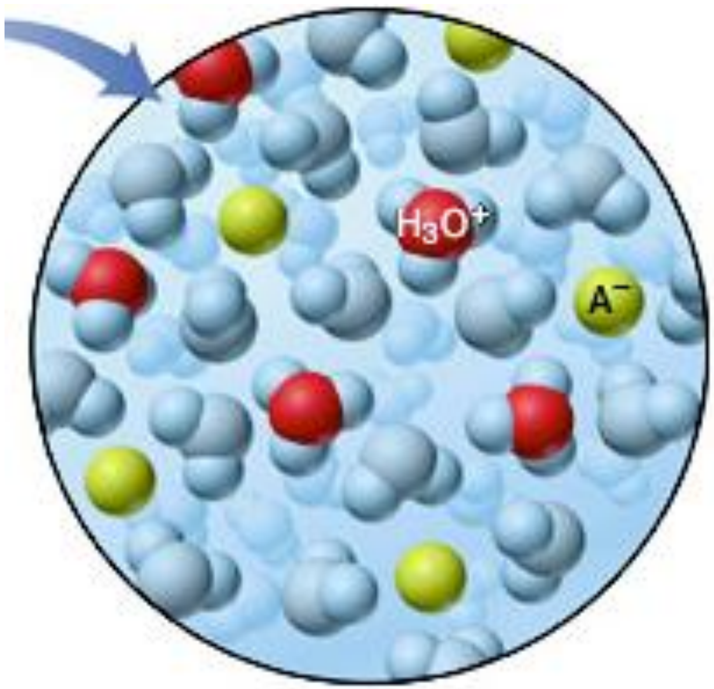
Strong Acids (exp. 7)

100% dissociation / good H^+ donor

equilibrium lies far to right

$HA \rightarrow H^+ + A^-$



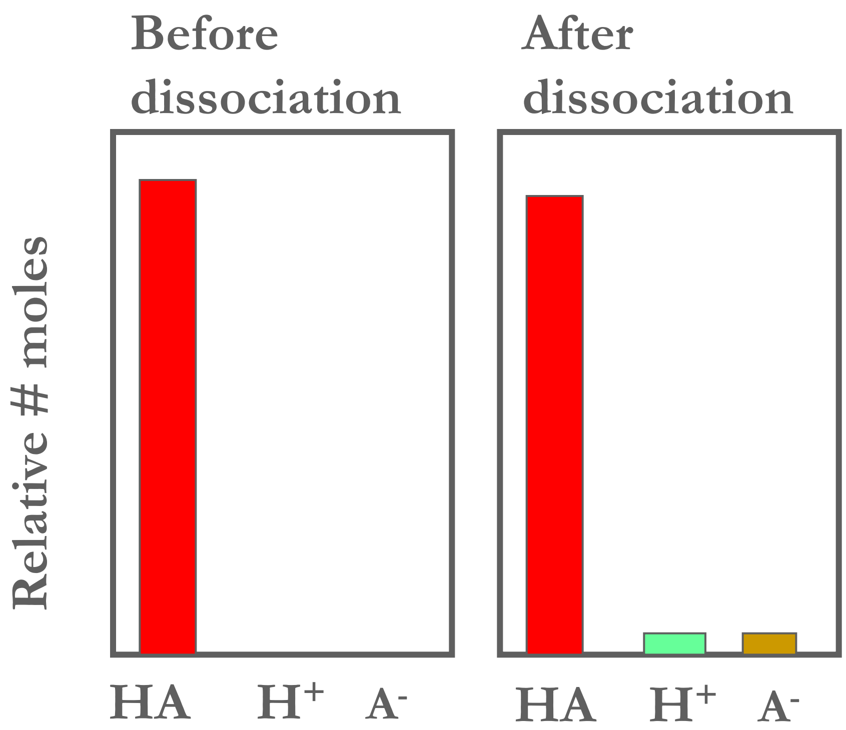


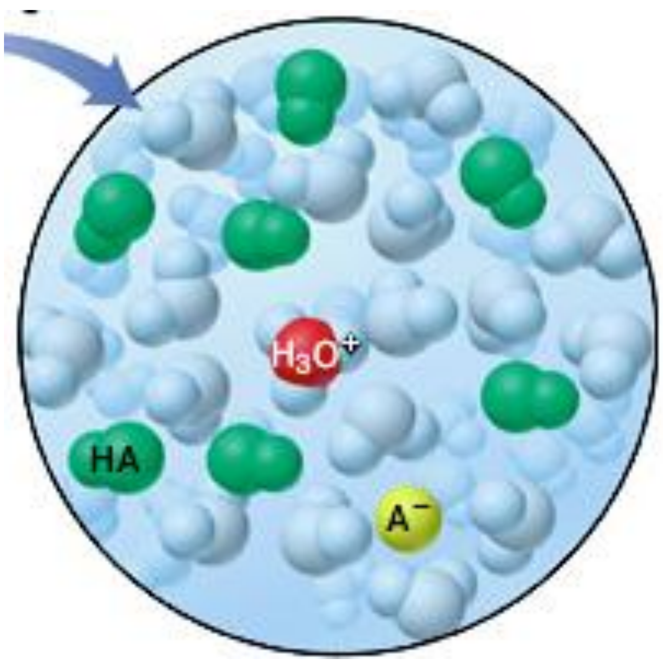
Weak Acids (exp. 13)

<100% dissociation / not-as-good H^+ donor

equilibrium lies far to left

$$HA \rightleftharpoons H^+ + A^-$$





Acid Dissociation Constant

For a weak acid:

$$HA \rightleftharpoons A^- + H^+$$

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$$

←amount dissociated

←amount undissociated

$$10^{-2} < K_a < 10^{-7}$$

$$2 < pK_a < 7$$

Henderson-Hasselbach Equation

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Smaller $K_a \rightarrow$ weaker acid
Larger $pK_a \rightarrow$ weaker acid

$$pK_a = -\log\left(\frac{[H^+][A^-]}{[HA]}\right)$$

$$\log(xy) = \log x + \log y$$

$$pK_a = -\log [H^+] - \log\left(\frac{[A^-]}{[HA]}\right)$$

$$-\log(x/y) = +\log (y/x)$$

$$pK_a = pH - \log\frac{[A^-]}{[HA]} \quad \textit{and}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

For buffer system only
considerable [HA],[A^-]

$[H^+]$, pH and K_a, $[A^-]$, $[HA]$

$$[H^+] = \frac{K_a[HA]}{[A^-]} \Rightarrow pH = pK_a + \log\frac{[A^-]}{[HA]}$$

1) $[A^-] < [HA] \rightarrow$ $\log\frac{[A^-]}{[HA]} < 0$ $\rightarrow pH < pK_a$

2) $[A^-] > [HA] \rightarrow$ $\log\frac{[A^-]}{[HA]} > 0$ $\rightarrow pH > pK_a$

3) $[A^-] = [HA] \rightarrow$ $\log\frac{[A^-]}{[HA]} = 0$ $\rightarrow pH = pK_a$

Chemical Equations

1) Weak acid **HA dissociation**

$$HA \rightleftharpoons A^{-} + H^{+}$$

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$$

2) Reverse of **water autoionization**

$$H^{+} + OH^{-} \rightleftharpoons H_2O$$

$$\boxed{\frac{1}{\mathrm{K_w}} = \frac{1}{[\mathrm{H^+}][\mathrm{OH^-}]} = \frac{1}{1\times 10^{-14}}}$$

Chemical Equations

3. **HA** neutralization with strong base, **NaOH**:

$$HA \rightleftharpoons A^- + H^+ \quad K_a$$

$$+ \quad OH^- + H^+ \rightleftharpoons H_2O \quad 1/K_w$$

$$HA + OH^- \rightleftharpoons A^- + H_2O \quad K_{neutralization}$$

$$\boxed{K_{neut} = \frac{[A^-]}{[HA][OH^-]} = \frac{K_a}{K_w}}$$

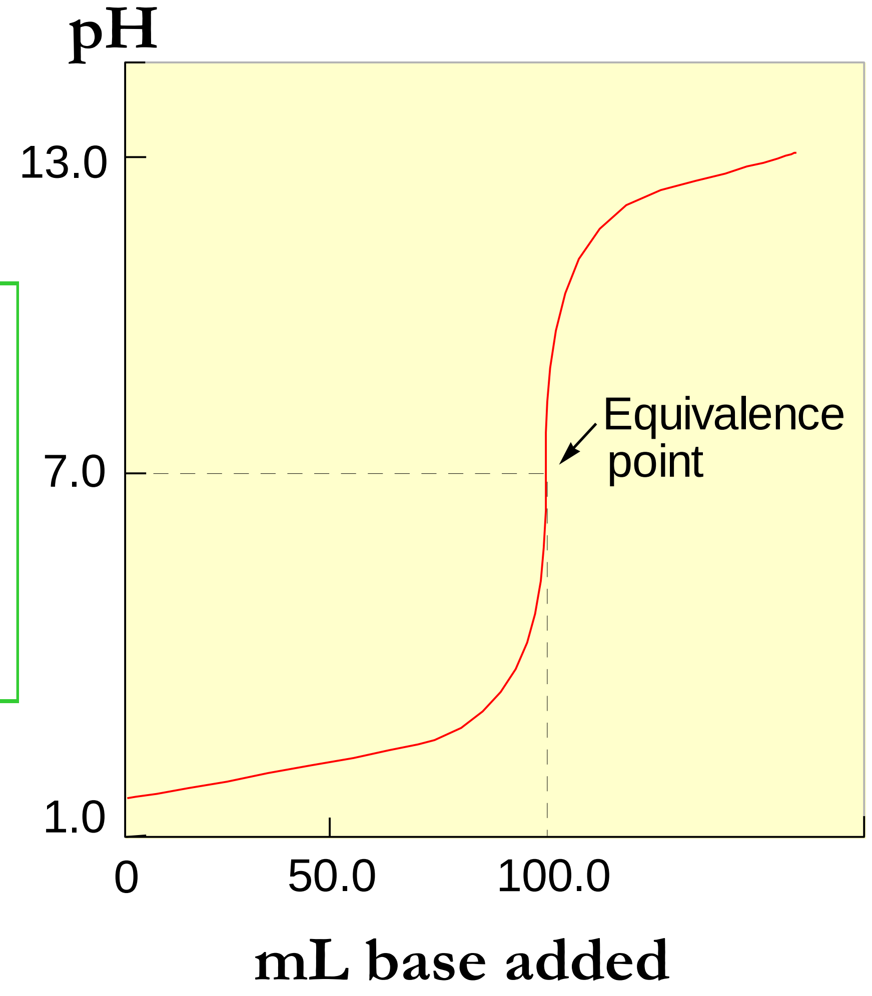
Strong acid-strong base titrations

At equivalence point, V_{eq}:

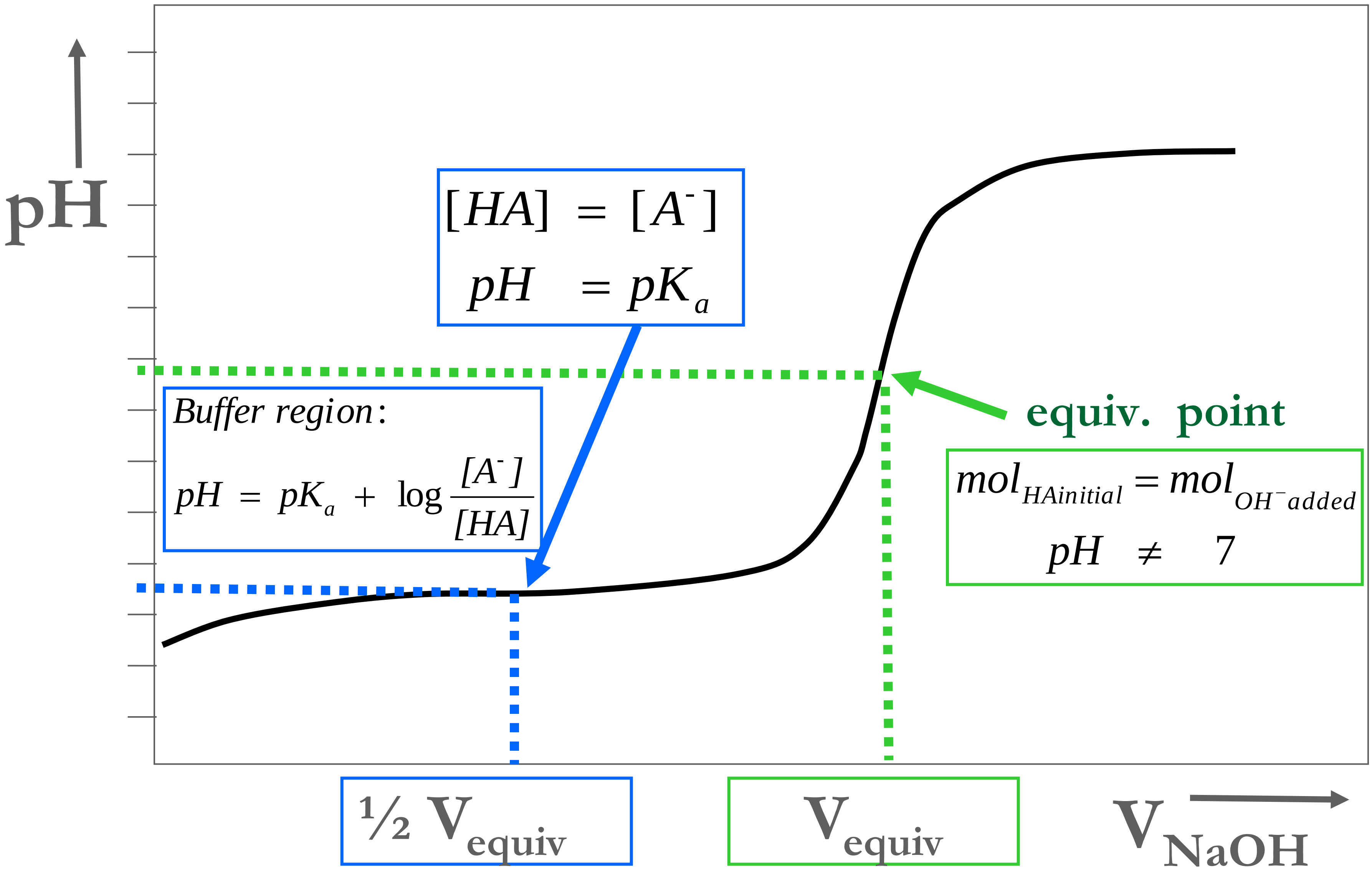
$$mol\ H^{+} = mol\ OH^{-}$$

$$n_{HA_{initial}} = n_{OH^{-}_{added}}$$

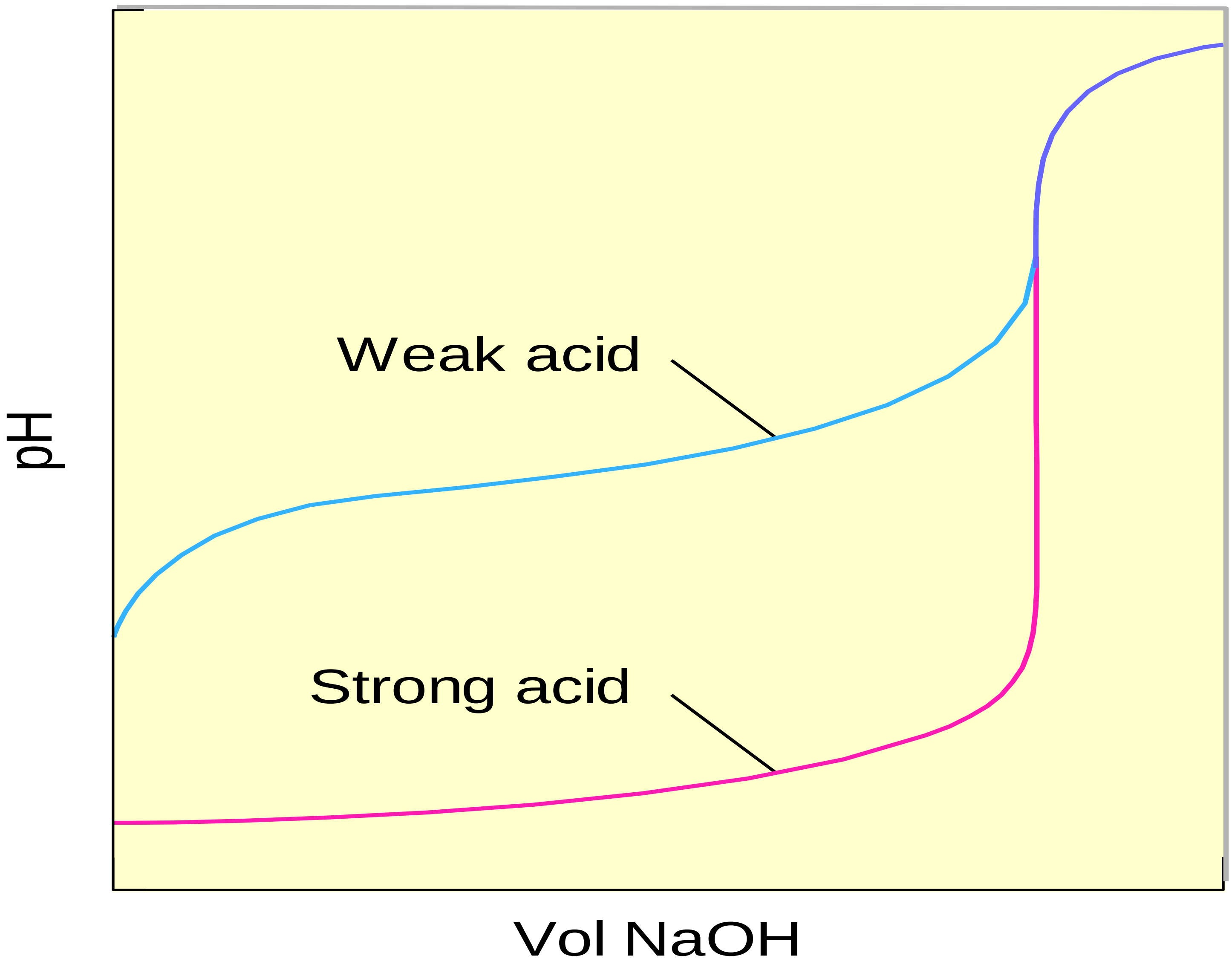
$$n_{HA_{initial}} = V_{OH^{-}_{added}} \times M_{OH^{-}_{added}}$$



Weak acid-strong base titrations



Differences in pH curves



Buffer Characteristics

- Contain relatively large amounts of weak acid and corresponding base.
- Added H^+ reacts to completion with weak base, A^-.
- Added OH^- reacts to completion with weak acid, HA.
- pH is determined by ratio of concentrations of weak acid and weak base.

Key points on the pH curve

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

1) **½ V_{equil}**

$$[HA] = [A^-]$$
$$pH = pK_a \neq 7$$

2) **V_{equil}**

$$mol_{OH^- added} = mol_{HA initial}$$
$$n_{OH^- added} = n_{HA initial}$$
$$V_{OH^- added} \times M_{OH^- added} = n_{HA initial}$$
$$pH \neq 7$$

Example Titration Curve

$\frac{1}{2}V_{eq}$ ~ 8.6 mL

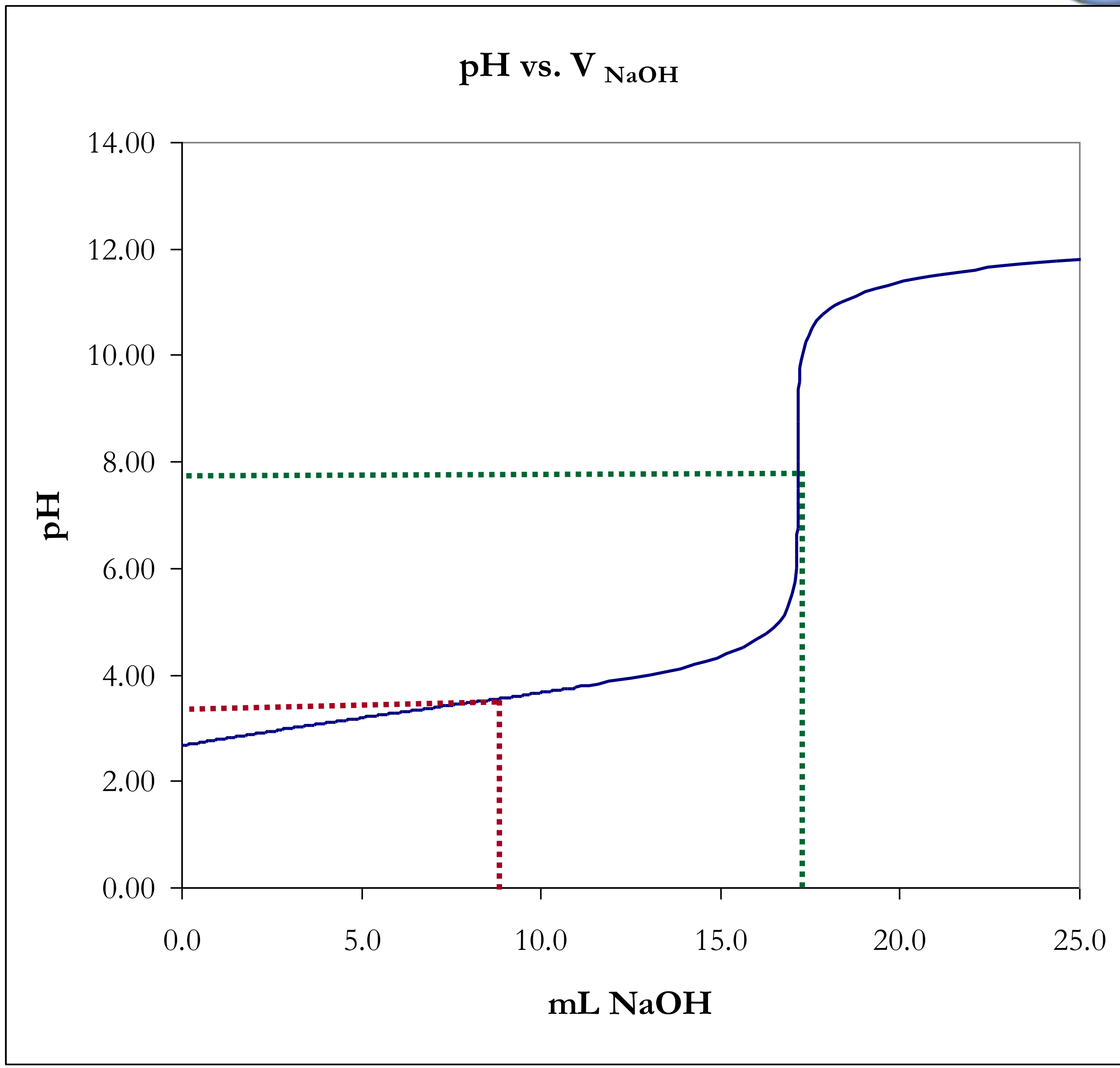
pH ~ 3.5

pK_a ~ 3.5

V_{eq} ~ 17.2 mL

pH ~ 7.8

n_{HA} ~ 1.7 10^{-3}



Does neutralization go to completion?

HA neutralization with strong base, **NaOH**:

$$HA \rightleftharpoons A^- + H^+ \qquad K_a$$

$$+ \quad OH^- + H^+ \rightleftharpoons H_2O \qquad 1/K_w$$

$$HA + OH^- \rightleftharpoons A^- + H_2O \qquad K_{neutralization}$$

$$\boxed{K_{neut} = \frac{[H^+][A^-]}{[HA]} \times \frac{1}{[H^+][OH^-]} = \frac{[A^-]}{[HA][OH^-]} = \frac{K_a}{K_w}}$$

Goes to completion ($10^7 < K_{neut} < 10^{12}$)

Example from text